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HEATS OF COMBUSTION OF ANTHRACITE COKES AND OF ARTIFICIAL AND NATURAL GRAPHITES[1]

By Phillip H. Dewey[2] and D. Roberts Harper, 3d[3]

ABSTRACT

There have been determined the heats of combustion of 30 samples of anthracite coke of known different temperatures of preparation (900° to 1,300° C), hydrogen contents (0.08 to 0.78 percent), and adsorptive capacities (0.13 to 37.5 cm^3 of gaseous CO_2 per gram of solid carbon), in order to study the effect of these properties on the energy content of the material. Data were also obtained on the heats of combustion of two samples of pure ash-free artificial graphite and four different samples of natural graphite.

The heats evolved, expressed in international kilojoules, for the combustion of 1 mole of solid carbon to form CO_2, at 25.0° C and a pressure of 1 atmosphere, without the production of external work, are as follows: Artificial graphite No. 0, 393.39 ±0.17; artificial graphite No. 1, 393.25 ±0.15; Ticonderoga natural graphite, 393.32 ±0.11; Buckingham natural graphite, 393.35 ±0.13; Baffin Island natural graphite, 393.37 ±0.26; and hydrogen-free anthracite coke, 403.03 ±0.29 (obtained by linear extrapolation to zero hydrogen content of the data on the hydrogen-containing cokes).

CONTENTS

I. INTRODUCTION

The heats of combustion of samples of carbon from many different sources have been reported in the literature. The graphites used have been natural graphites [1, 2, 3, 4, 5, 6],[4] Acheson graphite [2, 5, 6, 7], and blast-furnace and pig-iron graphite [2, 8]. The "amorphous" carbons have been wood charcoal [3, 8], and gas carbons [1, 4, 6, 7]. The values reported range from 7,894 to 8,272 cal/g of carbon for "amorphous" carbon and from 7,842 to 7,932 cal/g of

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[1] In this and the following paper (RP1140) are presented the experimental results obtained in a cooperative investigation of the thermochemistry of carbon by the Coal Research Laboratory of the Carnegie Institute of Technology and by the National Bureau of Standards. The work described in this paper was performed at the former institution as part of the program of fundamental research on coal and derived products, under the direction of H. H. Lowry.

[2] Formerly at the Coal Research Laboratory of the Carnegie Institute of Technology, now with the Pittsburg Plate Glass Co.

[3] Formerly at the Coal Research Laboratory of the Carnegie Institute of Technology, now deceased.

[4] Figures in brackets throughout the text indicate the literature references at the end of this paper.

carbon for graphite. The present work was undertaken to obtain accurate data on heats of combustion of several samples of artificial and natural graphites and of various specially prepared anthracite cokes containing known different amounts of hydrogen, and to study the effect of the following factors on the energy content of the anthracite cokes: Thermal history, hydrogen content, adsorptive capacity, activity, and porosity.

II. MATERIAL

The benzoic acid used to calibrate the calorimeter was Standard Sample 39e from the National Bureau of Standards. It was pressed into pellets and weighed in the crucible in which it was to be burned.

The carbons used in the study of the effect of chemical and physical properties were anthracite cokes prepared and analyzed at the Bell Telephone Laboratories according to the procedure outlined by H. H. Lowry [9] and under his supervision. The hydrogen content (% of carbon + % of hydrogen = 100%) ranged from 0.08 to 0.78 percent. The charge was weighed in the crucible in which it was to be burned, placed in a vacuum desiccator over calcium chloride, and evacuated for 4 hours with a Cenco Hyvac pump to a pressure less than 0.01 mm Hg. A liquid-air trap filled with activated charcoal was placed between the pump and desiccator to prevent the possibility of oil vapors backing up from the pump and being adsorbed by the sample. The necessity for this was shown by the fact that when there was no trap, the heat of combustion of the sample increased with time of evacuation, the increase being as much as 280 j/g of carbon. The vacuum was broken by admitting dry nitrogen through the second liquid-air trap connected between the desiccator and the activated charcoal trap. The sample was weighed again and immediately placed in the bomb.

The artificial graphite was spectroscopically pure graphite furnished by the National Carbon Co. in sticks 0.6 cm in diameter and 30 cm long, each piece wrapped in Cellophane. It is reported to have only 5 parts per million of impurities. Half of each stick was pulverized with an agate mortar and pestle to pass 150-mesh platinum gauze. Care was taken that the graphite was not contaminated in any way by coming in contact with any organic material other than the Cellophane in which it was wrapped.

The four samples of natural graphite were obtained from Ward's Natural Science Establishment, Rochester, N. Y., and are designated by the location where found. The specimens ranged in size from approximately 100 g to 1 kg, and all specimens consisted of well-defined crystals. In preparing the samples for combustion, approximately 20 g of the best crystals were cut out of the specimen, broken up in an agate mortar (all pieces of rock were thrown out), and ground for 36 hours in a porcelain mill with flint pebbles. Approximately 40 percent of the material passed a 150-mesh screen, and the size distribution showed that the grinding was attrition rather than impact grinding. After sifting the graphite, the particles smaller than 150 mesh were sealed in an evacuating system consisting of a liquid-air trap and a Cenco Hyvac pump and evacuated for 6 hours at 225° C.

The oxygen used was commercial atmospheric oxygen obtained in steel tanks at a pressure of 1,800 pounds. It was passed through a purifying train consisting of high-pressure bombs at room temperature, containing silica gel, Hopcalite catalyst, palladized asbestos, Ascarite, and Anhydrone, to remove traces of combustible material, carbon dioxide, and moisture. This purifying train was tested from time to time to check its effectiveness. At no time could any combustible material or carbon dioxide be detected in the issuing oxygen.

III. APPARATUS AND METHOD

The bomb was a regular Parr illium bomb chamber with a specially built two-valve stainless-steel head patterned after that of the Kroeker-Peters bomb used by Dickinson [10]. The bomb capacity was 390 cm^3. The gas inlet beyond the inlet valve was extended to within about 25 mm of the bottom of the bomb by means of a 2.5-mm platinum tube. About 6 mm above the end of the tube was welded a platinum-ring crucible support. The tube served to introduce the oxygen below the crucible to prevent disturbing the charge. Approximately 13 mm above the ring a 1-mm platinum wire, which served as ground lead for the firing fuse, was welded to the tube. The other firing lead consisted of a 1.5-mm platinum rod extending to within approximately 25 mm of the ring, terminating in about 25 mm of No. 22 (0.64 mm) platinum wire for manipulation. The fuse was a 9.0-mm length of 0.15-mm pure platinum wire and the charge of carbon was fired in every case without the addition of an auxiliary substance.

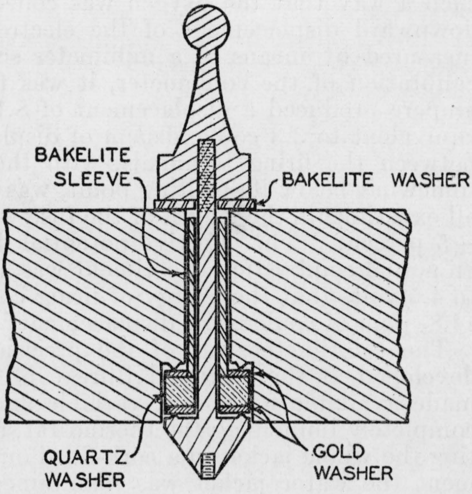

FIGURE 1.—*Method of insulating the firing pin.*

All oxidizable substances were eliminated from the interior of the bomb. The gasket between the bomb chamber and the head was pure gold, and the firing pin through the head was insulated from it by means of a quartz washer made tight with a pure gold gasket on either side. (See fig. 1.) The crucibles used with benzoic acid and the roasted anthracites were platinum and that used with the graphites was Vitreosil.

In order to obtain complete combustion of the roasted anthracites, a platinum crucible simulating a grate was used. The pure platinum crucible, 1 mm thick, had a rounded bottom, drilled with 0.5-mm holes over the entire bottom and up the sides to within 3 mm of the top, with a spacing of approximately 450 holes per square inch. Into this was pressed a 38-mm square of pure platinum 150-mesh gauze on which rested the 60 to 80-mesh sample. In this way a supply of oxygen to each particle of carbon was assured, smothering of the flame by carbon dioxide and/or ash was prevented, and the necessity of the use of asbestos mats to obtain complete combustion was avoided, thereby eliminating indeterminate heats of reaction due to slagging of asbestos and mineral matter in the carbon samples.

When this arrangement was tried with the graphite samples, the electrical conductivity of the graphite caused such a leakage loss to the grounded platinum crucible that the firing-energy measurement was rendered valueless. It was found that if the graphite was powdered very finely, to pass through 150-mesh platinum gauze, and burned in a Vitreosil crucible, it could be ignited with 2 to 8 j of firing energy, with practically complete combustion and with very little fusion of the ash with the Vitreosil.

The firing energy was obtained from an 18-volt lead storage battery. An oxygen coulometer, in series with the fuse wire, was arranged in such a way that the oxygen was collected in a narrow tube by the downward displacement of the electrolyte, the displacement being measured by means of a millimeter scale behind the tube. In the calibration of the coulometer, it was found that a current of 0.772 ampere produced a displacement of 8.18 cm in 35 seconds, which is equivalent to 3.3 coulombs/cm of displacement. The potential drop between the firing terminals, with the fuse wire at a temperature somewhat below its melting point, was measured to be 4.5 volts. In all experiments the length of the fuse wire was the same within about ±5 percent. The effective potential drop in the firing operation in an actual combustion experiment was assumed to be sufficiently near to 4.5 volts that the energy of firing could be taken as (3.3) (4.5) or 14.8_5 j/cm of coulometer displacement.[5]

The calorimeter was of the precision type patterned after that developed at the National Bureau of Standards by Dickinson [10], made available for use at variable and high room temperatures by completely immersing the thermostat, adding a cooling coil, and putting the whole jacket in a cork-filled outer jacket. During an experiment the water jacket was maintained at a temperature of 25.00° ±0.01° C.

The calorimeter temperature rise was measured by means of a Leeds & Northrup calorimetric-type platinum-resistance thermometer used in conjunction with a Leeds & Northrup resistance thermometer bridge (Mueller type) and a Weston galvanometer giving a deflection of about 1 mm for a resistance change of 0.0001 ohm. The initial and final temperatures were 23.70° C and approximately 25.9° C, respectively. Since the temperature rise during the calibration experiments corresponded to within ±0.15° C of that of the combustion experiments, the relation between the resistance of the thermometer and temperature is necessary only in determining the absolute temperature of the reaction and in checking the resistance for constancy. The fundamental interval was determined several times during the work with the results listed below:

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[5] Accurately, the firing energy is the integral, over the time of firing, of *EIdt*, where *E* and *I* are the values of the voltage and current at a time *t*. The coulometer actually measures the integral of *Idt* over the time of firing, and, therefore, in the above procedure, the firing energy is only evaluated correctly if *E* is constant. Examination of the data shows that in some experiments the firing energy was 20 or 30 times that in others. Since experiments where arcing inside the bomb was more than momentary, as evidenced by the reading of an ammeter in the firing circuit, were discarded at once, the difference in firing energy in the other experiments was most probably due to differences in the time required to start the reaction. If the firing current was insufficient to melt the fuse wire, the assumption that the effective value of *E* was 4.5 volts appears reasonable. At any rate, the results of the experiments in which the calculated firing energy was large are not significantly different from those in which it was small, and the results are, therefore, not inconsistent with foregoing assumption as to the average effective value of *E*.

Date	R_0 (ohms)	$R_{100}-R_0$ (ohms)
10/22/34	25.39795	9.94315
5/20/35	25.39803	9.94328
12/2/35	25.39801	9.94356

The mass of the sample was determined by direct weighing, and the weight of carbon dioxide formed in the combustion was determined by absorption in Ascarite and weighing [11]. This latter value was used to determine the amount of reaction and therefore was used in calculating the heats of combustion, since the carbons used contained various amounts of ash, unknown amounts of adsorbed moisture and gases, and known different amounts of hydrogen. The analytical train consisted of a modified U-tube containing lead peroxide distributed on asbestos fiber and maintained at a temperature of 218° C by boiling naphthalene, followed by a phosphorus pentoxide drying tube and three Ascarite U-tubes. On calibrating the lead peroxide tube, it was found that the tube increased in weight by 70 to 75 percent of the weight of nitric acid passed into it, the reaction corresponding to

$$PbO_2+2\ HNO_3 \longrightarrow Pb(NO_3)_2+H_2O+1/2\ O_2,$$

wherein 73 percent of the weight of HNO_3 is retained as $Pb(NO_3)_2$, since 1 mole of H_2O and 0.5 mole of O_2 are given off for each 2 moles of HNO_3 taken up. The first Ascarite tube absorbed the carbon dioxide, the second served as a check tube, and the third was used as a counterpoise in weighing. The analytical train was followed by a flowmeter and a bubble tube containing palladium chloride to test for carbon monoxide. In only one case was any carbon monoxide found, although the test was determined to be sensitive to an absolute quantity of 0.05 cm^3 of carbon monoxide. Determination of the carbon dioxide formed in the combustion of benzoic acid in the calibration runs was used to check the analytical train.

The energy equivalent of the calorimeter was determined by several combustions of benzoic acid and checked by a benzoic acid combustion after every specimen of roasted anthracite (three combustions) and graphite (four combustions). The calorimetric determinations were carried out essentially according to the procedure outlined by Dickinson [10].

No attempt was made to have exactly the same mass of water in the calorimeter, but a "standard" calorimeter was decided upon, and any deviation from this was determined and added as a correction to the energy equivalent as calculated to give a "standard" energy equivalent. In addition to the calorimeter can and thermometer, the "standard" calorimeter consisted of: Bomb, 3566.16 g; water inside bomb, 1.00 g; crucible, 4.84 g; charge, 1.16 g of benzoic acid; oxygen, 14.50 g; and water, 2872.00 g. The weight of water was not allowed to vary from 2,872 g by more than 0.5 percent (with one or two exceptions) and the difference in weight of any of these quantities was determined to the nearest 0.01 g, all weighed in air against brass weights. This difference times the energy equivalent of the substance per ohm change of resistance of the thermometer gives the correction to the determined energy equivalent.

One gram of water was placed in the bomb to saturate the space with water vapor at the beginning of the experiment. The air initially in the bomb was flushed out by filling with oxygen to 50 atmospheres and then releasing to atmospheric pressure. The bomb was then filled to 30 atmospheres and allowed to stand, to a depth of several centimeters, in water at about 60° C for 1 minute to make sure the space within the bomb was completely saturated with water vapor.

The observed temperature rise was corrected for heat transfer between calorimeter and jacket, and heat of stirring by Dickinson's method [10].

After the calorimetric determinations, the bomb was placed in a water bath and, by means of a high-pressure stainless-steel connection and a steel-to-glass ground joint, slowly discharged through the analytical train. During the discharge, which required approximately 1½ hours, the water bath was warmed to approximately 60° C, and after the pressure had reached atmospheric pressure, the bomb was flushed with oxygen (free of carbon dioxide and water) for 2 hours. This left the bomb flushed free of all carbon dioxide, water, and nitric acid. The naphthalene bath was removed from the lead peroxide tube and the tube allowed to cool with the oxygen still flowing, after which the tubes were wiped and weighed, closed to the atmosphere. The lead peroxide tube was closed by means of cork stoppers which were removed during weighing.

IV. CALIBRATION EXPERIMENTS

The energy equivalent of the calorimeter is given by

$$K_{t_m}=\frac{A_{t_n}\cdot a+14.85d+1315c}{t_n-t_0},$$

where K_{t_m} is the energy equivalent of the calorimeter in joules per unit rise of temperature, at the mean temperature; A_{t_n} is the heat of combustion per gram mass of benzoic acid at the final temperature, and a is the mass of sample in grams; d is the difference in centimeters in the coulometer readings before and after firing, and the constant 14.85j/cm serves as a multiplier to give the firing energy in joules; c is the increase in weight of the lead peroxide tube in grams and the constant 1,315 j/g serves as a multiplier to give the correction for the formation of nitric acid; and t_n-t_0 is the corrected temperature rise or increase in resistance of the thermometer in ohms. The heat of formation of aqueous nitric acid, according to the reaction, $1/2\ H_2O\ (liq)+1/2\ N_2\ (g)+5/4O_2\ (g)=HNO_3\ (aq,\ 0.005\ M)$, is taken as $-\Delta U=60.5$ kj/mole.

In table 2 are given the results of 42 calibration combustions, using 26,418 NBS int. j/g (mass) as the value for the heat evolved on the combustion of benzoic acid at 25.9° C, the final temperature, under the standard conditions of the bomb process, that is, when the initial oxygen pressure is 30 atmospheres and the masses of benzoic acid and water placed in the bomb are 3 g/liter of bomb volume [12]. This mass of benzoic acid under these conditions gives a "temperature" rise of 0.220 ohm for the "standard" calorimeter.

The energy equivalent of the calorimeter is expressed in international joules per ohm increase in resistance of the given platinum resistance thermometer at the given mean temperature of the experiments, and the calorimeter is thus used merely as a comparator between benzoic acid and carbon [14]. The amount of reaction in the calibration experiments was determined from the mass of benzoic acid burned. The sample was weighed in air against brass weights. Data and calculations for a typical calibration combustion are given in table 1.

TABLE 1.—*Data sheet for the combustion of benzoic acid, National Bureau of Standards Sample 39e*

Experiment 76–29. [Jacket temperature 25.00° C] Date 9/16/35.

Fore period		Middle period		After period	
t_1	R_1	t_m	R_m	t_2	R_2
10:20:02	27.7700	10:35:00	Fire	10:43	27.99387
35	02	08	Start	44	374
21:10	04	16	27.785	45	362
45	06	24	.81	46	350
22:20	08	32	.85	47	339
55	10	47	.90	48	327
23:30	12	36:15	.95	54	251
24:05	14	37:05	.98	55	239
40	16	38:00	.99	56	226
25:14	18	39	.9930	57	213
49	20	40	375		
10:30:27	27.7736	41	400		
31:03	38	42	396		
37	40				
32:13	42				
49	44				
33:24	46				
59	48				
34:35	50				

$\Delta R_1 = 0.0048$ ohm.
$\Delta t_1 = 840$ sec.
$\dfrac{\Delta R_1}{\Delta t_1} = 5.71 \times 10^{-6}$.

$t_m = 10{:}35{:}54$
(obtained from curve)

$\Delta R_2 = -0.00174$ ohm.
$\Delta t_2 = 840$ sec.
$\dfrac{\Delta R_2}{\Delta t_2} = 2.07 \times 10^{-6}$

Wt of crucible 4.83766 g.
Crucible+sample 5.99160 g.
Wt of sample 1.15394 g.
Corr. to vac 0.00085 g.
Mass of sample 1.15479 g.

Coulometer
11.15 cm
11.40 cm
0.25 cm

Wt of bomb before filling with O_2+16.40 g=3591.40 g
Wt of bomb after filling with O_2+ 4.03 g=3591.40 g
Wt of oxygen=12.37 g

bomb =3575.00 g
bomb+O_2 =3587.37 g
Wt of can, etc.= 760.63 g
Wt of calorimeter without water=4348.00 g

Wt of counterpoise=7224.40 g
Wt of calorimeter as used+ 1.95 g=counterpoise.
Wt of calorimeter as used=7222.45 g
Wt of calorimeter without water=4348.00 g
Wt of water=2874.45 g

Barometer	Temperature
743.8 mm	22.6° C
742.4 mm	23.4° C

Ascarite tubes

No. 18(120)	No. 50	No. 44	PbO_2
5.75270 g	5.47440 g	6.71230 g	5.38764 g
5.75238 g	5.47438 g	9.62477 g	5.38964 g
−32 g [a]		2.91247 g	0.00200 g
		Corr. to vac 131 g	
		2.91378 g	

at 10:34:35 $R_1 = 27.77500$ ohms.
$79 \times \dfrac{\Delta R_1}{\Delta t_1} =$ 45 ohms.
at $t_m = 10{:}35{:}54$ $R_1 = 27.77545$ ohms.

at 10:43:00 $R_2 = 27.99387$ ohms.
$426 \times \dfrac{\Delta R_2}{\Delta t_2} =$ 88 ohms.
at $t_m = 10{:}35{:}54$ $R_2 = 27.99475$ ohms.
$R_1 = 27.77545$ ohms.
$t_n - t_o = \Delta R =$ 0.21930 ohms.

Actual energy equivalent at t_m.

$$K_{t_m} = \frac{A_{t_n} . a + 14.85d + 1{,}315c}{t_n - t_o}$$

$$= \frac{(26{,}418 \times 1.15479) + (14.85 \times 0.25) + (1315 \times 0.002)}{0.21930} = 139{,}141 \text{ int.j/ohm.}$$

	Standard calorimeter	Actual calorimeter	Diff.	Energy equivalent per gram	Correction
Bomb	3566.16 g	3568.01 g	+1.85 g	0.45 j/deg.	−0.84 j/deg
Crucible	4.84 g	4.84 g	0 g	----------	----------
Charge	1.16 g	1.16 g	0 g	----------	----------
O_2	14.50 g	12.37 g	−2.13 g	.730 j/deg.	+1.55 j/deg
H_2O	2872.00 g	2874.45 g	+2.45 g	4.175 j/deg.	−10.21 j/deg
					−9.50 j/deg

Correction [b] in joules per ohm$= -950/(dR/dT)_{25} = -950/0.1001 = -94.9$ j/ohm.
Standard energy equivalent=139,141−95=139,046 (at t_m=24.80° C).

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[a] Change in weight of counterpoise due to change of buoyancy of air.
[b] δ for this thermometer was taken as 1.48, which gives $(dR/dT)_{25} = 0.1001$ ohm/deg.

The data for the anthracite cokes and the graphites were worked up in the same manner.

TABLE 2.—*Results of the calibration experiments with benzoic acid National Bureau of Standards Sample 39e*

[Average mean temperature, 24.80° C]

Experiment	Mass of sample	Energy liberated by sample	Energy of formation of HNO_3	Energy of firing	Total energy liberated	Temperature rise	Energy equivalent of calorimeter	Weight of water	Correction to standard calorimeter	Standard energy equivalent of calorimeter
	g	*Int. j*	*Int. j*	*Int. j*	*Int. j*	*Ohms*	*Int. j/ohm*	*g*	*Int. j/ohm*	*Int. j/ohm*
57-51	1.15744	30577.2	9.62	5.94	30592.8	0.22028	138,881	2867.70	+178	139,059
57-65	1.13417	29962.5	7.70	4.77	29975.0	.21547	139,114	2874.00	−79	139,035
57-79	1.14263	30186.0	8.37	10.37	30204.7	.21724	139,038	2872.10	−5	139,033
57-81	1.16596	30802.3	10.54	5.19	30818.0	.22147	139,152	2873.62	−70	139,082
57-87	1.14496	30247.6	6.61	5.19	30259.4	.21716	139,341	2878.69	−274	139,067
57-91	1.16178	30691.9	8.16	5.94	30706.0	.22083	139,048	2872.25	−5	139,043
57-99	1.15993	30643.0	5.65	6.40	30655.1	.22288	137,541	2838.00	+1,392	138,933
69-9	1.14847	30340.3	6.69	6.61	30353.6	.21803	139,218	2876.80	−200	139,018
69-25	1.16239	30708.0	7.86	35.68	30751.5	.22146	138,898	2866.90	+207	139,065
69-33	1.15584	30535.0	7.40	4.43	30546.8	.21940	139,229	2876.95	−207	139,022
69-47	1.16290	30721.5	10.79	5.94	30738.2	.22130	138,898	2869.05	+121	139,019
69-55	1.19458	31558.4	7.53	5.19	31571.1	.22729	138,902	2867.70	+173	139,075
69-63	1.13991	30114.1	8.16	6.65	30128.9	.21708	138,792	2866.05	+244	139,036
69-73	1.19609	31598.3	6.07	6.69	31611.1	.22779	138,773	2862.30	+400	139,173
69-81	1.16265	30714.9	3.43	6.69	30725.0	.22100	139,027	2871.60	+15	139,042
69-91	1.15031	30388.9	6.27	7.40	30402.6	.21916	138,723	2865.85	+252	138,975
69-99	1.14916	30358.5	8.70	6.53	30373.7	.21834	139,112	2872.85	−31	139,081
76-9	1.14864	30344.8	5.02	4.43	30354.2	.21888	138,680	2862.70	+363	139,043
76-11	1.15914	30622.2	3.43	6.99	30632.6	.22023	139,094	2872.85	−41	139,053
76-29	1.15479	30507.2	2.64	3.72	30513.6	.21930	139,141	2874.45	−95	139,046
76-43	1.15027	30387.8	0.46	3.72	30392.0	.21818	139,298	2878.50	−270	139,028
76-53	1.17310	30991.0	5.86	2.97	30999.8	.22248	139,337	2879.15	−296	139,041
76-61	1.15826	30598.9	7.20	8.16	30614.3	.22017	139,048	2873.25	+12	139,060
76-87	1.15700	30565.6	36.69	48.99	30651.3	.22089	138,763	2867.30	+260	139,023
76-89	1.15935	30627.7	2.76	3.72	30634.2	.22039	139,000	2873.30	+13	139,013
76-91	1.16720	30835.1	2.64	2.97	30840.7	.22207	138,878	2867.95	+233	139,111
81-3	1.16654	30817.7	3.72	2.97	30824.4	.22276	138,375	2857.45	+666	139,041
81-11	1.16426	30757.4	0.21	2.97	30760.6	.22029	139,637	2888.40	−613	139,024
81-15	1.16324	30730.5	8.28	3.72	30742.5	.22049	139,428	2883.60	−416	139,012
81-19	1.16779	30850.7	1.63	2.97	30855.3	.22148	139,314	2880.65	−290	139,024
81-27	1.15611	30542.1	0.33	2.22	30544.6	.22017	138,732	2866.95	+267	138,999
81-35	1.16167	30689.0	--------	2.22	30691.2	.22122	138,736	2867.00	+268	139,004
81-43	1.15843	30603.4	.54	3.72	30607.7	.21979	139,259	2879.00	−226	139,033
81-53	1.15778	30586.2	1.80	79.48	30667.5	.22063	139,000	2871.70	+75	139,075
81-61	1.15727	30572.8	0.71	4.56	30578.1	.21954	139,282	2879.65	−252	139,030
81-69	1.15664	30556.1	.67	2.97	30559.7	.21936	139,313	2879.80	−260	139,053
81-77	1.15499	30512.5	2.76	4.43	30519.7	.21946	139,067	2874.05	−24	139,043
81-85	1.16046	30657.0	1.13	3.72	30661.8	.22004	139,346	2881.20	−316	139,030
81-93	1.15507	30514.6	0.63	4.43	30519.7	.22014	138,638	2863.60	+405	139,043
87-3	1.15609	30541.6	.21	2.97	30544.8	.21961	139,086	2872.90	+25	139,111
87-13	1.21894	32202.0	3.93	5.19	32211.1	.23140	139,201	2878.20	−196	139,005
87-21	1.16923	30888.7	10.29	47.69	30946.7	.22257	139,042	2871.45	+60	139,102
Mean										139,043
Uncertainty, equal to three times probable error of mean										12

V. COMBUSTION EXPERIMENTS ON CARBON

The combustion experiments were carried out in exactly the same manner as the calibration experiments, using the same "standard" calorimeter. The "actual" calorimeter differed a little in that the crucible was heavier and the charge was carbon instead of benzoic acid. These deviations were included in the correction from "standard" energy equivalent to "actual" energy equivalent. The "standard" energy equivalent used was the average of the 42 calibration experiments. After the first combustion of each sample, the mass of charge was adjusted to give the "standard" temperature rise, namely, 0.220 ohm.

The amount of reaction was determined from the mass of carbon dioxide formed in the combustion. This takes care of the presence of inert material in the sample and measures directly the amount of carbon burned.[6] The degree of precision of the analysis was checked in the calibration experiments by determining the amount of carbon dioxide formed in exactly the same way as in the combustion experiments on the carbons. The ratio of "CO_2 obtained" to "theoretical CO_2" from benzoic acid, using the atomic weights C=12.010, H=1.0078, and O=16.0000, is given in table 3.

Table 3.—*Analytical data on benzoic acid*

Experiment	Theoretical mass of CO_2	Ratio: $\frac{\text{Determined } CO_2}{\text{Theoretical } CO_2}$
	g	
57-51	2.91993	1.00046
57-65	2.86123	0.99991
57-79	2.88257	1.00017
57-81	2.94142	1.00036
57-87	2.88845	0.99999
57-91	2.93088	1.00003
57-99	2.92621	1.00048
69-9	2.89730	1.00007
69-25	2.93242	1.00039
69-33	2.91589	1.00049
69-47	2.93370	1.00025
69-55	3.01363	0.99985
69-63	2.87571	1.00031
69-73	3.01743	0.99980
69-81	2.93307	1.00043
69-91	2.90194	1.00038
69-99	2.89904	1.00021
76-9	2.89773	1.00022
76-11	2.92422	1.00038
76-29	2.91324	1.00019
76-43	2.90184	1.00048
76-53	2.95944	1.00009
76-61	2.92200	1.00033
76-87	2.91882	1.00047
76-89	2.92475	1.00053
76-91	2.94455	1.00013
81-3	2.94289	1.00046
81-11	2.93714	1.00066
81-15	2.93456	1.00016
81-19	2.94604	1.00029
81-27	2.91657	1.00040
81-35	2.93060	1.00063
81-43	2.92243	1.00037
81-53	2 92079	1.00053
81-61	2.91950	1.00045
81-69	2.91791	1.00030
81-77	2.91375	1.00078
81-85	2.92755	1.00056
81-93	2.91395	1.00049
87-3	2.91652	0.99992
87-13	3.07508	1.00040
87-21	2.94967	1.00007
Average		1.00029

1. ANTHRACITE COKES

In table 4 are given the heats of combustion of 30 samples of anthracite coke on each of which three combustions were made. These cokes were prepared at six different temperatures, ranging from 900° to 1,300° C, thereby giving cokes with six different hydrogen contents, since the hydrogen content of a given sample of coke depends on the thermal treatment to which it has been subjected [9]. The adsorptive capacity, x/m, in cubic centimeters of carbon dioxide absorbed per gram of carbon at 0° C and 760 mm Hg, and porosity, P, in cubic millimeters per gram, from which the activity, A, equal to $(x/m)/P$ is calculated, had been determined for each sample at the Bell Telephone Laboratories [13]. The details of these measurements may be found in the work referred to.

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[6] Except when the sample contains carbonate. See, for example, p. 482, of the following paper.

TABLE 4.—*Heats of combustion of anthracite cokes*

[Average mean temperature, 24.80° C]

Experiment	Sample	x/m	P	A	Mass before evacuation	Mass of carbon dioxide formed	Temperature rise	Weight of water	Deviation from standard energy equivalent	Energy equivalent of calorimeter	Energy of formation of HNO_3	Energy of firing	Heat of combustion under conditions of bomb process [1]	Average [2]	
TEMPERATURE OF PREPARATION 900° C; HYDROGEN CONTENT 0.78 PERCENT															
		cm^3/g	*mm^3/g*	*cm^3/mm^3*	*g*	*g*	*Ohms*	*g*	*Int. j/ohm*	*Int. j/ohm*	*Int. j*	*Int. j*	*Int. j/g* of C	*Int. j/g* of C	*cal/g* of C
57-53	123	34.58	71.5	0.482	0.93756	3.03869	0.20643	2872.95	−106.3	138,937	9.5	17.8	34,554	34,553	8259.7
57-55					1.00195	3.24933	.22071	2873.90	−54.8	138,988	13.0	20.8	34,557		
57-57					1.00109	3.24770	.22155	2870.20	−216.7	138,826	14.2	124.7	34,547		
76-3	147	37.22	81.0	.460	1.0002	3.22775	.21909	2872.50	−103.3	138,940	14.8	4.8	34,536	34,506	8248.5
76-5					1.0119	3.17496	.21512	2877.35	+88.3	139,131	17.7	8.9	34,513		
76-7					1.0213	3.29970	.22382	2873.70	−50.2	138,993	22.5	48.9	34,469		
81-79	150	37.5	84.0	.446	0.96464	3.13263	.21215	2879.75	+152.3	139,195	9.1	57.9	34,465	34,475	8241.1
81-81					1.00122	3.22707	.21920	2872.20	−160.2	138,883	11.7	63.8	34,484		
81-83					1.00221	3.23701	.21951	2870.25	−257.7	138,785	7.9	3.0	34,475		
Group average [3]														34,511 ±26	8249.8 ±6.3
TEMPERATURE OF PREPARATION 1,000° C; HYDROGEN CONTENT 0.49 PERCENT															
69-93	146	12.56	30.8	0.408	0.9997	3.24567	0.21743	2881.80	+278.6	139,322	20.2	82.4	34,085	34,094	8150.0
69-95					1.0015	3.24122	.21607	2891.25	+688.2	139,731	17.0	15.9	34,096		
69-97					1.0031	3.24662	.21741	2877.10	+80.7	139,124	16.0	17.1	34,102		
69-75	113	15.14	32.0	.473	1.0208	3.35356	.22532	2872.30	−119.2	138,924	14.0	77.1	34,105	34,101	8151.7
69-77					0.9903	3.24874	.21815	2873.25	−67.4	138,976	16.3	86.1	34,081		
69-79					.9954	3.26788	.21913	2882.50	+310.0	139,353	16.2	94.2	34,118		
69-57	108	22.20	57.3	.387	1.00082	3.25566	.21808	2883.90	+380.3	139,423	18.2	54.2	34,142	34,143	8161.7
69-59					1.01068	3.28339	.22031	2874.05	−46.0	138,997	15.9	16.8	34,140		
69-61					1.00940	3.27895	.22038	2870.10	−213.8	138,829	11.8	28.2	34,147		
69-83	145	22.58	59.9	.377	1.0012	3.26678	.22005	2872.10	−130.1	138,913	16.6	69.8	34,192	34,153	8164.1
69-85					1.0059	3.27356	.21965	2881.15	+263.5	139,307	17.2	109.9	34,110		
69-87					1.0052	3.27817	.22025	2879.10	+166.1	139,209	14.8	90.4	34,156		
69-35	102	27.00	67.7	.399	0.94615	3.07049	.20564	2882.00	+328.8	139,372	19.5	85.0	34,080	34,087	8148.4
69-37					1.00955	3.28069	.22001	2871.15	−170.7	138,872	13.8	14.1	34,096		
69-39					1.01137	3.28769	.21889	2899.70	+1031.2	140,074	19.8	59.4	34,086		
69-43	103	32.05	85.4	.375	1.00115	3.15279	.21201	2862.40	−538.0	138,505	23.4	102.9	33,983	33,998	8127.1
69-45					1.04118	3.28380	.21989	2874.90	−12.5	139,031	17.7	88.4	33,997		
69-49					1.04098	3.27745	.21965	2875.55	+15.5	139,059	24.8	96.6	34,015		
69-67	112	33.45	93.5	.358	1.0213	3.26875	.21923	2873.80	−56.1	138,987	16.1	101.8	34,026	34,018	8131.9
69-69					1.0263	3.28549	.22011	2868.55	−277.8	138,765	14.3	14.1	34,035		
69-71					0.9752	3.12801	.20953	2875.75	+36.4	139,079	21.8	103.3	33,992		
Group average														34,085 ±25	8147.9 ±6.0

TEMPERATURE OF PREPARATION 1100° C; HYDROGEN CONTENT 0.28 PERCENT

76-63	164	5.74	25.8	0.222	0.99067	3.35316	0.22332	2868.85	−312.9	138,730	10.1	8.9	33,837	33,859	8093.8
76-65					.98305	3.32082	.22161	2865.35	−406.2	138,637	8.6	16.4	33,874		
76-67					.97697	3.30689	.22103	2866.35	−422.9	138,620	10.4	68.3	33,865		
76-55	162	7.91	30.5	.259	1.00103	3.35301	.22281	2884.60	+424.2	139,467	7.9	66.8	33,879	33,878	8098.4
76-57					0.97008	3.30821	.22040	2887.00	+446.4	139,489	0.3	111.3	33,930		
76-59					.99144	3.32083	.22049	2878.40	+101.7	139,145	9.1	18.6	33,824		
76-35	84	13.32	60.9	.219	1.00280	3.33345	.22285	2874.20	−36.8	139,006	12.4	53.5	33,981	33,980	8122.8
76-41					0.9885	3.29032	.21944	2876.60	+89.1	139,132	7.8	12.6	33,980		
76-47	85	23.08	89.0	.259	.95612	3.14044	.20949	2877.35	+143.5	139,187	6.4	58.6	33,947	33,923	8109.1
76-49					1.01157	3.33037	.22127	2888.95	+995.3	140,038	11.2	77.3	33,899		
Group average														33,902 ±32	8104.1 ±7.8

TEMPERATURE OF PREPARATION 1,150° C; HYDROGEN CONTENT 0.21 PERCENT

81-87	152	0.13	5.0	0.026	1.00056	3.45744	0.22970	2878.20	+87.0	139,130	4.3	78.0	33,784	33,785	8076.2
81-89					0.96062	3.30745	.21950	2874.30	−73.2	138,970	8.3	8.2	33,778		
81-91					.96111	3,31591	.21870	2896.55	+849.6	139,893	6.1	7.4	33,795		
69-27	151	0.20	5.5	.036	.96010	3.31507	.21999	2875.00	+37.6	139,081	12.9	43.8	33,758	33,760	8070.2
69-29					.96146	3.30886	.21998	2867.30	−334.2	138,709	14.6	14.4	33,760		
69-31					.96221	3.32218	.22072	2874.80	−17.6	139,025	8.5	69.8	33,761		
69-3	97	1.82	8.1	.227	.96655	3.32280	.22149	2870.60	−194.9	138,848	13.2	86.2	33,806	33,810	8082.1
69-5					.96175	3.30499	.21991	2875.35	+4.6	139,048	10.0	81.6	33,802		
69-7					.96187	3.29501	.21992	2866.75	−357.7	138,685	12.5	75.8	33,821		
69-11	101	4.19	16.4	.255	.96206	3.29350	.21934	2871.90	−142.2	138,091	11.5	83.2	33,792	33,788	8076.9
69-13					.96534	3.30808	.22050	2868.35	−290.7	138,752	14.4	84.5	33,784		
69-15					.95984	3.28528	.22053	2847.50	−1,166.7	137,876	10.8	102.8	33.788		
81-63	106	6.04	66.2	.091	.94779	3.21941	.21385	2877.30	+38.9	139,082	6.6	27.5	33,815	33,850	8091.7
81-65					.94783	3.25374	.21602	2881.35	+220.9	139,264	10.0	8.2	33,861		
81-67					.94782	3.25666	.21659	2878.55	+99.1	139,142	15.4	17.8	33,873		
57-85	98	10.67	42.1	.253	.96549	3.30311	.21959	2875.25	+29.3	139,072	11.9	13.4	33,847	33,832	8087.4
81-95					.95995	3.28587	.21910	2866.05	−419.6	138,623	8.6	21.5	33,838		
81-97					.96053	3.28087	.21823	2873.74	−102.9	138,940	5.9	6.6	33,852		
81-99					.95989	3.29269	.21925	2882.90	+275.3	139,318	12.3	155.9	33,791		
Group average														33,806±16	8081.2±3.9

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[1] The amount of reaction was determined from the mass of carbon dioxide formed. 44.010/12.010 g of carbon dioxide was taken as equivalent to 1 g of carbon.

[2] 1 calorie equals 4.1833 int. j. (See ref. 14.)

[3] The error given is equal to three times the probable error of the mean.

TABLE 4.—*Heats of combustion of anthracite cokes*—Continued

[Average mean temperature, 24.80° C]

Experiment	Sample	x/m	P	A	Mass before evacuation	Mass of carbon dioxide formed	Temperature rise	Weight of water	Deviation from standard energy equivalent	Energy equivalent of calorimeter	Energy of formation of HNO_3	Energy of firing	Heat of combustion under conditions of bomb process	Average	
TEMPERATURE OF PREPARATION 1,200° C; HYDROGEN CONTENT 0.15 PERCENT															
		cm³/g	*mm³/g*	*cm³/mm*	*g*	*g*	*Ohms*	*g*	*Int. j/ohm*	*Int. j/ohm*	*Int. j*	*Int. j*	*Int. j/g of* C	*Int. j/g of* C	*cal/g of* C
81-13	166	0.76	7.3	0.104	0.96185	3.33164	0.22064	2880.60	+188.2	139,231	6.4	7.4	33,773	33,776	8074.0
81-17					.96126	3.32067	.22002	2886.70	+435.5	139,479	8.2	77.3	33,770		
81-49					.96127	3.32457	.22074	2882.70	+277.4	139,320	7.7	94.5	33,785		
81-71	174	1.37	9.5	.144	1.00168	3.45730	.22907	2882.50	+273.6	139,317	8.6	10.4	33,805	33,796	8078.8
81-73					.96489	3.31184	.22037	2877.70	+66.5	139,109	3.0	126.3	33,775		
81-75					.93616	3.22591	.21538	2871.10	−222.1	138,821	4.7	133.6	33,807		
76-79	81	10.74	52.5	.205	.95280	3.27447	.21837	2867.40	−358.5	138,685	11.3	92.8	33,774	33,813	8082.9
76-97					.96163	3.30884	.21974	2879.65	+140.6	139,184	12.8	22.2	33,832		
76-99					.96182	3.31411	.22090	2871.10	−210.8	138,832	11.3	58.6	33,832		
81-5	82	12.50	81.8	.153	.96322	3.30582	.22031	2870.95	−218.4	138,825	7.2	63.9	33,824	33,823	8085.2
81-7					.96052	3.29418	.21929	2871.45	−206.7	138,836	5.9	34.2	33,806		
81-9					.96081	3.30253	.21978	2873.10	−165.2	138,878	12.5	11.9	33,840		
81-21	180	14.16	117.4	.120	.96332	3.28185	.21787	2879.95	+159.4	139,202	13.9	14.8	33,832	33,848	8091.2
81-23					.97550	3.31538	.22120	2865.25	−466.4	138,577	8.1	16.3	33,854		
81-25					.90927	3.10015	.20652	2875.25	−40.2	139,003	7.7	54.2	33,859		
Group average														33,811±16	8082.4±3.6

TEMPERATURE OF PREPARATION 1,300° C; HYDROGEN CONTENT 0.08 PERCENT

57-89	195	0.30	6.0	0.050	0.96360	3.36254	0.22308	2873.55	−72.8	138,970	7.9	33.5	33,739	33,721	8060.9
57-93					.95084	3.31304	.21945	2884.00	+362.3	139,405	17.9	92.9	33,714		
57-97					.95337	3.31986	.22067	2878.75	+143.5	139,187	13.0	159.0	33,711		
81-55	201	2.04	31.1	.066	.96160	3.39566	.22455	2886.35	+428.4	139,471	12.3	40.8	33,739	33,727	8062.3
81-57					.94085	3.31794	.21901	2884.90	+355.6	139,399	8.7	11.4	33,696		
81-59					.94060	3.32763	.22002	2883.55	+312.9	139,356	9.5	6.7	33,746		
81-29	197	5.73	31.2	.184	.96076	3.33681	.22053	2874.60	−48.9	138,994	10.8	24.4	33,624	33,640	8041.5
81-31					.96131	3.34169	.22178	2871.30	−205.4	138,838	6.9	111.3	33,636		
81-33					.96078	3.34243	.22147	2870.90	−230.5	138,813	8.6	32.6	33,660		
81-37	198	7.88	47.7	.165	.96135	3.31611	.21945	2874.70	−21.8	139,021	6.4	63.8	33,636	33,609	8034.1
81-39					.96537	3.34286	.22147	2865.15	−471.0	138,572	5.5	87.5	33,540		
81-41					.96163	3.32715	.21997	2879.15	+124.7	139,168	8.4	51.9	33,650		
81-45	199	8.76	71.9	.122	.96128	3.33517	.22169	2874.95	−58.6	138,984	7.2	140.6	33,692	33,662	8046.8
81-47					.95344	3.31382	.21948	2878.10	+82.4	139,125	13.2	110.7	33,630		
81-51					.95277	3.32488	.22004	2877.20	+31.0	139,074	6.9	49.8	33,665		
Group average														33,672±29	8049.1±6.9

To determine the effect of hydrogen content on heat of combustion, Q, a linear relation was fitted to the experimental values by the method of least squares. This gave $Q=33{,}590+110{,}400\ m_H/m_C$ international joules per gram of carbon, where m_H/m_C is the ratio of the mass of hydrogen to the mass of carbon in the sample. There is an uncertainty of 6,000 in the coefficient of m_H/m_C and an uncertainty of 23 in the value of Q at $m_H/m_C=0$, the uncertainty being taken as three times the probable error. The average and maximum differences between the observed values and those given by the equation are, respectively, 44 and 148 j/g of carbon. Figure 2 is a plot of heat of combustion against hydrogen content, showing the experimental values and the fitted line; the dashed curves show the uncertainty in the position of the line (calculated as above).

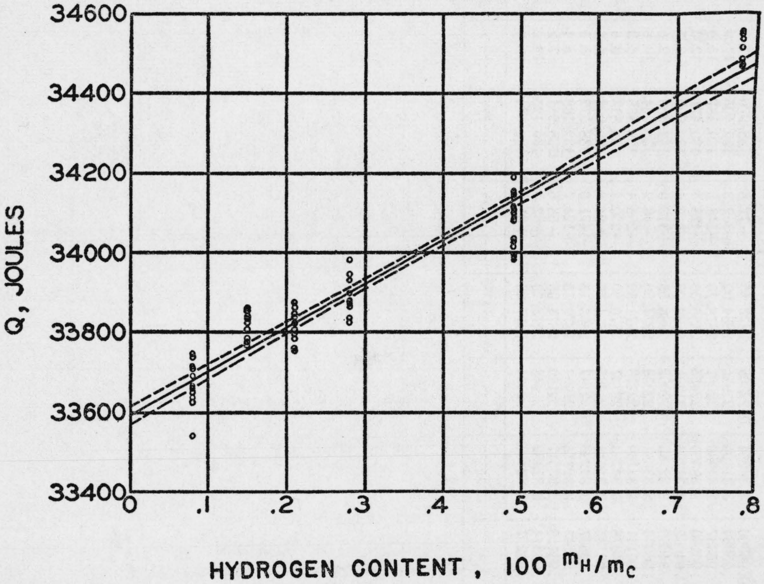

FIGURE 2.—*Plot of the heat of combustion of the anthracite cokes, as a function of the hydrogen content.*

The scale of ordinates gives the heat of combustion of the anthracite coke, in international joules per gram of carbon, for the bomb process at 25° C. The scale of abscissas gives 100 times the value of m_H/m_C, the ratio of the mass of hydrogen to the mass of carbon in the anthracite coke.

Figure 3 is a plot of the heat of combustion against adsorptive capacity, x/m, for the various samples of anthracite coke. From this plot it appears that there is no definite relation between heat of combustion and adsorptive capacity, for cokes of a given hydrogen content. To test this result, the dependence of Q on hydrogen content and adsorptive capacity simultaneously was investigated by fitting a linear relation to the observed values by the method of least squares. This gave $Q=33{,}591+110{,}600\ m_H/m_C-0.061\ x/m$ international joules per gram of carbon. The uncertainty (three times the probable error) in the coefficient of x/m is here ± 2.19, which is 36 times its own value. Hence it may be concluded that adsorptive capacity has relatively little effect on the heat of combustion for given values of hydrogen content, and that the effect of adsorptive capacity may be neglected in comparison with errors arising from impurities or other causes. The same appears to be true for porosity, *P*, and activity, *A*.

In view of this fact, it may be stated that, within the limits of uncertainty of the data, the heats of combustion of these samples of anthracite cokes are dependent only on hydrogen content, as given by the previously stated relation, $Q=(33{,}590\pm23)+(110{,}400\pm6000)$ $m_{\mathrm{H}}/m_{\mathrm{C}}$ international joules per gram of carbon. It may be pointed out that the coefficient of $m_{\mathrm{H}}/m_{\mathrm{C}}$ is considerably less than the 140,000 int. j (33,500 cal) per gram of hydrogen, which would be obtained if the heat of combustion of the hydrogen in the cokes were equal to the heat of combustion of gaseous hydrogen. The significance of this difference probably lies partly in the fact that the experimentally determined coefficient includes contributions of other physical or chemical properties of the cokes which may affect their heats of combustion.

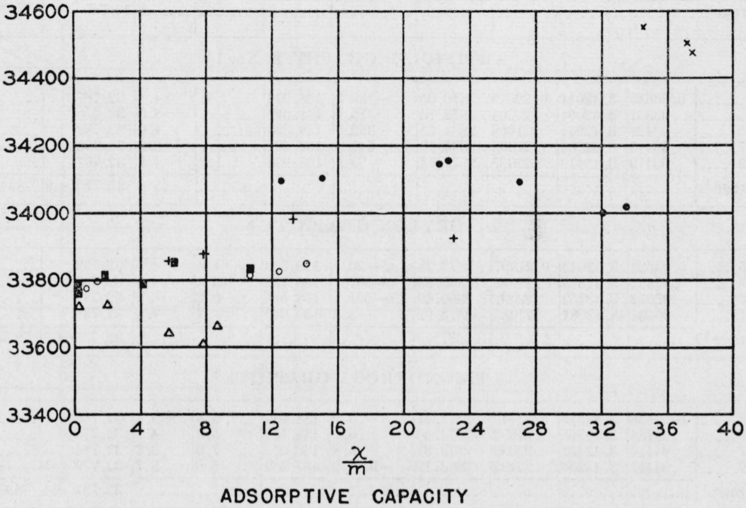

FIGURE 3.—*Plot of the heat of combustion of the anthracite cokes, of various given hydrogen contents, as a function of the adsorptive capacity.*

The scale of ordinates gives the heat of combustion of the anthracite coke, in international joules per gram of carbon, for the bomb process at 25° C. The scale of abscissas gives the value of the adsorptive capacity, *x/m*, which is the volume in milliliters of carbon dioxide adsorbed per gram of carbon at 0° C and a pressure of 760 mm Hg. The symbols indicate the following temperatures of preparation and hydrogen contents, respectively: ×, 900° C, 0.78 percent of H; ●, 1,000° C, 0.49 percent of H; +, 1,100° C, 0.28 percent of H; ■, 1,150° C, 0.21 percent of H; ○, 1,200° C, 0.15 percent of H; △, 1,300° C, 0.08 percent of H.

2. ARTIFICIAL AND NATURAL GRAPHITES

For comparison with the heat of combustion of carbon in the anthracite cokes obtained by extrapolation to zero hydrogen content, similar calorimetric data were obtained for two samples of artificial graphite and for four samples of natural graphite. The data are given in table 5, and descriptions of the different graphites are given in the footnotes of the table.

TABLE 5.—*Heats of combustion of artificial and natural graphites*

[Average mean temperature=24.8° C.]

Experiment	Mass of sample before evacuation	Mass of carbon dioxide formed	Temperature rise	Weight of water	Correction from "standard" energy equivalent	Energy equivalent of calorimeter	Energy of formation of nitric acid	Energy of firing	Heat of combustion under conditions of the bomb process, per gram of *carbon* burned[6]	
	g	*g*	*Ohms*	*g*	*j/ohm*	*Int. j/ohm*	*j*	*j*	*Int. j*	*cal*
ARTIFICIAL GRAPHITE No. 0[1]										
76-71	0.93516	3.42670	0.22139	2859.37	−586.1	138,457	0.8	4.4	32,774	
76-73	.93462	3.42340	.21933	2888.72	654.7	139,698	.3	3.7	32,793	
76-93	.93566	3.42713	.22060	2873.64	20.5	139,063		3.7	32,798	
76-95	.93398	3.42157	.22057	2867.23	−248.1	138,795		4.4	32,782	
Average[7]									32,787 ±11	7837.6 ±2.6
ARTIFICIAL GRAPHITE No. 1[1]										
87-5	0.93339	3.42014	0.22019	2870.05	−129.3	138,914		4.4	32,767	
87-9	.93367	3.42064	.22004	2872.75	−15.9	139,027		3.0	32,770	
87-15	.93427	3.42244	.21968	2881.55	352.7	139,396		4.9	32,782	
87-17	.93413	3.42204	.21938	2886.19	548.8	139,592		3.0	32,790	
87-19	.93419	3.42419	.22035	2871.71	−59.8	138,983	1.3	4.5	32,767	
Average[7]									32,775 ±9	7834.7 ±2.2
CEYLON GRAPHITE[2]										
87-25	0.93523	3.32943	0.21397	2872.78	−20.5	139,023	1.4	4.5	32,733	
87-27	.95862	3.41393	.21988	2865.83	−307.1	138,736	3.4	4.9	32,735	
87-29	.96252	3.42452	.22092	2860.59	−527.5	138,515	0.2	6.2	32,738	
87-31	.96134	3.42081	.21985	2873.02	−3.3	139,040	.7	7.4	32,736	
Average[8]									32,735 ±2	7825.2 ±0.5
TICONDEROGA GRAPHITE[3]										
87-43	0.95638	3.48515	0.22440	2871.77	−59.0	138,984	3.4	3.7	32,785	
87-45	.93784	3.40365	.21892	2874.56	60.2	139,103	5.0	4.9	32,776	
87-47	.94116	3.42431	.22039	2873.31	8.8	139,052	7.0	3.4	32,784	
87-49	.94117	3.42200	.22292	2833.12	−1684.2	137,359	5.9	3.7	32,779	
Average									32,781 ±4	7836.2 ±1.0
BUCKINGHAM GRAPHITE[4]										
87-53	0.93532	3.40147	0.21888	2873.75	25.9	139,069	4.8	4.4	32,784	
87-55	.94171	3.42359	.22047	2871.79	−55.6	138,987	6.1	4.4	32,790	
87-57	.94167	3.42113	.22022	2873.39	10.5	139,053	5.1	4.4	32,790	
87-59	.94060	3.41774	.21999	2871.94	−49.8	138,993	5.4	5.2	32,773	
Average									32,784 ±8	7836.8 ±1.9
BAFFIN ISLAND GRAPHITE[5]										
87-33	0.96171	3.44619	0.22196	2870.61	−105.4	138,938	4.4	4.4	32,784	
87-35	.96106	3.44440	.22171	2872.91	−7.9	139,035	2.1	2.1	32,789	
87-37	.95593	3.42705	.22056	2874.75	67.4	139,110			32,807	
87-39	.94868	3.40527	.21910	2871.85	−55.6	138,987	4.4	4.4	32,760	
Average									32,785 ±20	7836.8 ±4.7

[1] Two samples of spectroscopic-grade graphite from the National Carbon Co. reported to contain only 5 parts per million of impurities.

[2] Sample was approximately a 50-g lump, very uniform, and definitely, although irregularly, crystalline. Contained 2.2 percent of ash. Material passing 150-mesh contained 2.3 percent of ash; material not passing 150-mesh contained 2.2 percent of ash.

[3] Sample was approximately a 100-g lump, uniform and definitely crystalline. Ash = 0.33 percent. Material passing 150-mesh contained 0.38 percent of ash; material not passing 150-mesh contained 0.30 percent of ash.

[4] Sample was an approximately 1-kg lump of very definite columnar structure, the crystals being about 1.5 to 2 cm long in three distinct layers. The crystals were flat and needle-like. Material passing 150-mesh contained 0.25 percent of ash; material not passing 150-mesh contained 0.11 percent of ash.

[5] Sample was an approximately 250-g lump consisting of very well defined crystals. Ash = 4.1 percent. Material passing 150-mesh contained 1.7 percent of ash; material not passing 150-mesh contained 0.44 percent of ash.

[6] The amount of reaction was determined from the mass of carbon dioxide formed. 44.010/12.010 g of carbon dioxide was taken as equivalent to 1 g of carbon.

[7] The average for the two samples of artificial graphite is 32,780 ±8 int. j, or 7835.9 ±1.9 cal/g of carbon.

[8] See p. 482 of the RP 1140 regarding this low value for Ceylon graphite.

After grinding and sifting, that material which passed through 150-mesh platinum wire gauze was used for the measurements. It is to be noted that the heats of combustion per gram of carbon for the artificial, Ticonderoga, Buckingham, and Baffin Island graphites are, respectively, 32,780, 32,781, 32,784, and 32,785 int. j, and on the average differ by about 2.4 percent from the value 33,590 int. j obtained for the heat of combustion per gram of carbon in the anthracite cokes. The low value for Ceylon graphite is explained in the following paper (p. 482).

These values are in terms of the bomb process, which is a constant-volume process at an initial pressure of 30 atmospheres. In order to reduce these to $-\Delta U_R$, the heat of reaction under standard conditions for the pure reaction

$$C_{(s,\ 1\ \mathrm{atm})} + O_{2(g,\ 1\ \mathrm{atm})} \longrightarrow CO_{2(g,\ 1\ \mathrm{atm})},$$

the reaction taking place without the production of external work, the reduction eq 81 of Washburn [12] is used. This Washburn reduction amounts to -0.379 int. kj/mole for pure carbon under the conditions of this work. Using this correction, the values of $-\Delta U_R$, the heat of the reaction in international kilojoules of 1 mole of carbon under standard conditions at 25° C, are as follows: Artificial graphite No. 0, 393.39 ±0.17; artificial graphite No. 1, 393.25 ±0.15; Ticonderoga natural graphite, 393.32 ±0.11; Buckingham natural graphite, 393.35 ±0.13; Baffin Island natural graphite, 393.37 ±0.26; hydrogen-free anthracite coke, 403.03 ±0.29 (obtained by linear extrapolation to zero hydrogen content of the data on hydrogen-containing cokes).

The percentage uncertainty assigned to these final values is the total uncertainty defined as $\pm\sqrt{a^2+b^2+c^2}$ percent, where a is the percentage error assigned by Jessup and Green [12] for the value of the heat evolved when 1 g of benzoic acid is burned in the bomb (0.023%); b is the uncertainty in the energy equivalent of the calorimeter as given in table 2 (0.009%); and c is the uncertainty assigned to the final combustion experiments on the given sample of carbon, taken as three times the probable error of the mean and expressed in percent.

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